Redox-active phosphines: synthesis and crystal structures of palladium(II) complexes of a metallaphosphine in two different oxidation states.

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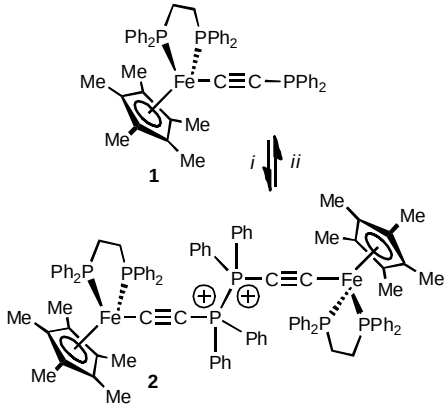
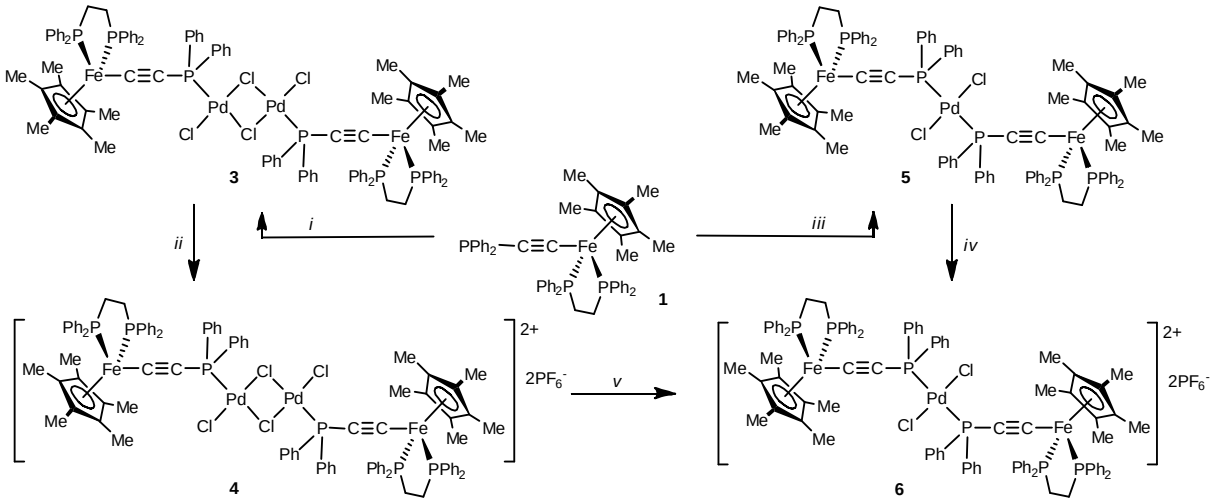
The redox- active metallaphosphine [Fe(dppe)(η^5-C_5Me_5) (C≡C-PPh_2)] reacts with [Pd(1,5-cod)Cl_2] give mono- and *bis*- phosphine complexes as a function of stoichiometry, and these complexes provide a stable redox- active platform which allows reversible one- electron {Fe(II)→ Fe^+(III)} oxidations within the palladium coordination sphere.

Fine control of architecture and the ability to generate quite specific electronic environments[1] means that phosphines are exceptionally widely used in many metal- catalysed processes,[2] and their versatility has driven recent research into areas as varied as self- assembling phosphines for enantioselection,[3] supramolecular phosphines allowing unprecedented catalytic selectivities,[4] and hybrid chemical/biological phosphine- containing systems.[5] However, there has been comparatively little recent interest in the class of redox- active phosphines,[6] which should constitute an unusual class of "non- innocent" ligands[7,8] and have been invoked *inter alia* for the switching of catalytic processes.[9] We have recently demonstrated that phosphorus centres and redox- active organoiron endgroups can communicate strongly if linked through molecular wires such as acetylenes, and that oxidation of the Fe(II) endgroup in **1** provokes significant reactivity at the phosphorus centres (Scheme 1).[10] This unusual behaviour prompted a study of the coordination chemistry of this metallaphosphine towards Pd(II) centres.



Scheme 1: Redox switching of metallaphosphine **1.** Reagents: *i:* [FcH][PF_6], 2 eq., CH_2Cl_2, 20ºC, 1h; *ii:* [$CoCp_2$] 3 eq., CH_2Cl_2, 20ºC, 1h.



Scheme 2: Coordination chemistry of **1** and redox reactivity of the resulting Pd(II) complexes **3** and **5**. Reagents and conditions: *i:* [$PdCl_2$(1,5-cod)] (1.0eq.), CH_2Cl_2, 15h, 97%; *ii:* [FcH][PF_6], CH_2Cl_2, 1h, > 98%; *iii:* [$PdCl_2$(1,5-cod)] (0.5eq.), CH_2Cl_2, 15h, 96%; *iv:* [FcH][PF_6], CH_2Cl_2, 1h, > 98%; *v:* Compound **2** (1.0eq.), CD_2Cl_2, 15mn, > 95%.

Reaction of the diamagnetic metallaphosphine **1** with one equivalent of [$PdCl_2$(1,5-cod)] gives a near- quantitative isolated yield of a blue, air-stable dimeric complex [Pd_2Cl_4(**1**)$_2$] **3** that shows a classical *trans*- phosphine configuration about a butterfly- configured Pd_2Cl_4 core (Fig 1, in purple).[11] The metalloligand undergoes moderate structural changes upon coordination, with the most significant differences being associated with the alkyne linker (Fig 1). The C≡C and C-P bond lengths in **3** are slightly longer and shorter respectively than those normally found for simple $PdCl_2$- coordinated alkynyl-(diaryl phosphines)[12] and the alkynyl $\nu_{C\equiv C}$ stretch falls from 1964 to 1930 cm^{-1}, all of which imply an increased contribution from an iron-vinylidene resonance hybrid.[13]

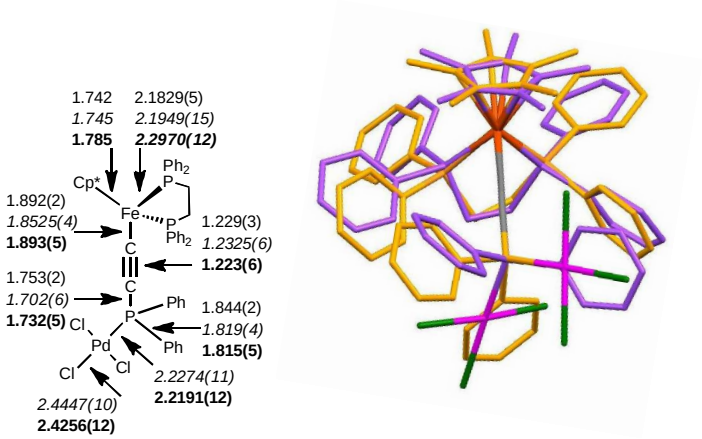


Fig 1. Left: Superimposed X-ray- structures showing one half of each of the dimers forming the **3**, **4** redox couple, showing ligand superstructure for the neutral complex **3** (purple) and its oxidation product **4** (gold). **(**Pd in magenta, Fe in orange, Cl in green)**.** See supplementary for individual depictions of these complexes. Right: X-ray structural changes upon passing from free ligand **1** (plain text) to neutral dimer **3** (*italic*) and dication **4** (**bold**). Values are averaged over chemically equivalent sites.

The cyclic voltammogram for **3** shows two closely spaced reversible oxidations at +0.16 and +0.25 V (both showing ΔEp = 85 mV in CH_2Cl_2 vs SCE), which lie within a well-precedented window for the organoiron endgroup;[13] bulk chemical oxidation using [FcH][PF_6][14] cleanly and near- quantitatively gave the black, air sensitive, dichloromethane-soluble **4**, whose formulation as the corresponding double oxidation product was confirmed by an X- ray structural analysis (Fig 1, gold). The crystallographic data confirm an essentially iron- based oxidation, which is reflected in an elongation of *a)* the mean Fe-P distances to the dppe ligand from 2.1949 to 2.2970 Å (+4.7%) and *b)* the mean Fe-$Cp^*_{centroid}$ distances from 1.745 to 1.785 Å (+2.2%).[15] The oxidation has a significantly smaller effect upon the palladium coordination sphere: a slight shortening of the mean Pd-P distance, from 2.2274(11) to 2.2191(12) Å (-0.4%) and a modest (0.8%) shortening in the *trans*- Pd-Cl distance from 2.4447(10) to 2.4256(12)Å are observed,[16] whilst the sum of the angles made by the organic groups at the Pd-coordinated phosphorus also rises only modestly from 317.6 to 321.8°. The dimeric palladium core of the molecule can be expected to act as "spacer" between the two oxidised [Pd(**1**$^+$)] components and an Evans determination[17] of a room temperature magnetic moment of 2.21±0.1 BM at 293K is consistent with a ditopic diradical featuring two non-interacting spins.[18]

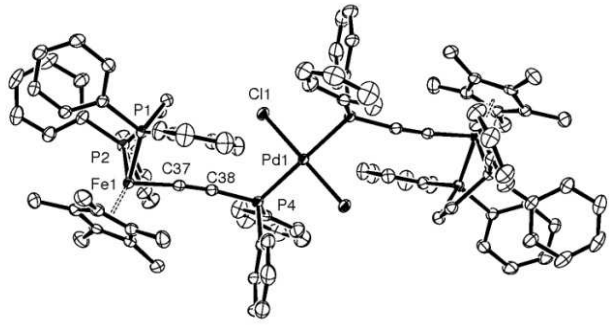


Fig. 2: X-ray structure of the neutral monomeric Pd complex **5.**

Palladium dimers of type **3** are excellent sources of both homo- and heteroleptic [$PdCl_2L_2$] complexes[19] and **5**, which offers the possibility of two- electron redox chemistry within a Pd coordination sphere, was found to be accessible through either reaction of two equivalents of **1** with the palladium bridged dimer **3**, or by simple reaction of two equivalents of **1** with [$PdCl_2$(1,5-cod)] (Scheme 2). Single crystals of the purple, air-stable *trans*- configured **5** revealed metallaphosphine ligands that are very similar to those in **3** and Pd-P distances (2.338(1)Å) which are normal for mutually *trans*- phosphine ligands in a Pd(II) complex (Fig. 2). DFT data from a model for **5**[20] (Fig. 3) show a sharp increase in the NBO- calculated positive charge at the Pd- bound phosphorus (+0.62) and a significant rise at the iron-coordinated alkyne carbon (+0.10) upon coordination but only negligible changes (<0.04) elsewhere. Again, cyclic voltammetry showed closely- spaced reversible oxidation waves ($E^1_{1/2}$ = –0.02 V, $E^2_{1/2}$ = 0.11 V) and chemical oxidation using two equivalents of [FcH][PF_6] provided a black, air-sensitive product, **6**. Crystals suitable for a diffraction study were not obtained, but comparison of the very similar ^{1}H NMR data for **4** and **6**,[21] and an Evans determination showing a value of 2.42 ±0.1 BM (298 K) that is again classical for two unpaired electrons,[18] imply a *bis*-Fe(III) complex showing little spin-spin coupling across the palladium centre. A DFT comparison of NBO charge distributions in models[14] for **5** and **6** confirms an iron based oxidation ($\delta Q_{Fe(5\rightarrow6)}$= +0.36) that causes significant changes in charge at the linker atoms ($\delta_{Q(Fe\text{-}\mathbf{C})}$= -0.13; $\delta_{Q(P\text{-}\mathbf{C})}$= +0.21) but significantly smaller effects at phosphorus and at palladium ($\delta_{Q(P,\ Pd)}$ < 0.02).

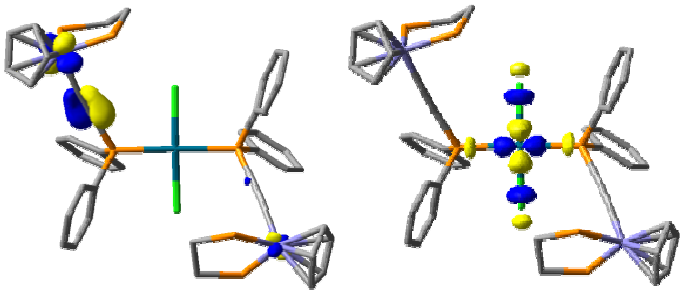
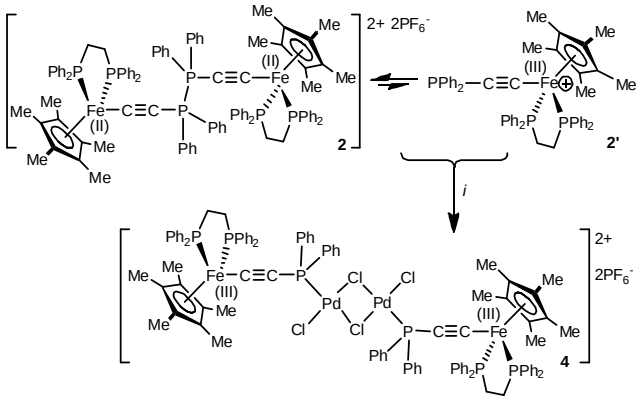


Fig 3: The B3PW91 calculated HOMO (left) and LUMO (right) for $[PdCl_2L_2]$, (L= $FeCp\{H_2PCH_2CH_2PH_2\}C_2PPh_2$), a model for **5**. Calculated HOMO- LUMO gap: 3.05eV.

The individual redox steps that occur within the bound couples **3**,**4** and **5**,**6** appear to be well-behaved, but the chemical reversibility of the system as a whole clearly also rests upon the integrity of the dissociated ligands. The stability of **1** is established but our previous study has shown that the iron (III) proligand **2'** normally exists as a 1,1'- (biphosphine)dication **2**[10] (Scheme 3); this raises the undesirable possibility of the transient dissociation of **4** with subsequent dimerisation of the Fe(III) ligand monomers to generate a 1,1'-(biphosphine)dication **2** reservoir and a ligand- deficient solution that deposits $[PdCl_2]$. Experiments conducted upon isolated 1,1'-(biphosphine)dication **2** and $[PdCl_2(1,5\text{-cod})]$ indicate that this mixture cleanly generates complex **4** (with 2eq of Pd) or **6** (with 1eq of Pd), and therefore confirm that ligand dissociation from both systems is reversible. The most likely mechanism involves the transient dissociation of the P-P bond to generate the Fe(III) proligand **2'**[10] prior to capture by the Pd centre (Scheme 3).



Scheme 3: Reaction of **2** with $[PdCl_2(1,5\text{-cod})]$ to generate the dicationic dimer **4.** Reagents and conditions: *(i)* $[PdCl_2(1,5\text{-cod})]$, 2 eq., CH_2Cl_2, 1h, 20 °C, >98%.

To conclude, metallaphosphines bearing $[Fe(\kappa^2\text{-dppe})(\eta^5\text{-}C_5Me_5)]$ endgroups bind to Pd(II) in both their neutral and cationic forms and can therefore be used to generate a chemically stable, redox- switchable coordination sphere about $PdCl_2$ centres. The $[Pd(II)\text{-}(\mathbf{1}^+)_2] \leftrightarrow [Pd(IV)^{2+}\text{-}(\mathbf{1})_2]$ valence tautomer is firmly shifted to the left, so the metallaligand brings a potential for varying the overall electron count of the complex without excessively

compromising the electronic identity of the palladium(II) centre. Reactivity studies of **3**-**6** are in progress.

Notes and references

† Electronic Supplementary Information (ESI) available: Full experimental, spectroscopic and crystallographic data. See DOI: 10.1039/c4dt00455h.

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[21] See supplementary. Note that the Cp* proton shifts in **4** : -8.5 and **6** : -8.7 ppm are both typical of [Fe^{III}(dppe)(C_5Me_5)]$^+$- groups.[13]